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Thesis

THE DETERMINATION OF CRYSTAL STRUCTURE BY MEANS OF X-RAYS

by

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TABLE OF SYMBOLS

a:b:c:	is the axial ratio of a crystal. The letters a,b,c are also used to designate unit lengths along the axes of reference
a_o, b_o, c_o	are the lengths of the sides of the unit cell of a crystal as measured along the x, y and z axes of coordinates respectively
α, β, γ	are the axial angles of a crystal
c	is the velocity of light
d_{hkl}	the spacing of geometrically like planes parallel to the possible crystal face (h k l)
(h k l)	the Miller indices of a possible crystal face
$(h\ k\ l)_n$	the Miller indices of a reflection from a plane (h k l) in the nth order.
θ	the angle of reflection for X-rays
2θ	the deviation of a diffracted beam of X-rays
λ	wave length
I	intensity
μ	absorption coefficient
N	number of electrons in an atom
n	the order of reflection
ν	frequency
r	radius of sphere of projection
p	density
V'	potential in volts
x', y', z'	are the Cartesian coordinates of a point

$x = \frac{x'}{a_o}$; $y = y'/b_o$; $z = z'/c_o$

INTRODUCTION

From time to time in the past possible arrangements which would not conflict with other known properties as cleavage, symmetry, or chemical properties, have been proposed for the atoms (or molecules) in crystals. With the discovery of the diffraction of X-rays and the use of the theory of space groups together with a group of postulates of generally admitted validity crystal strudtures can be deduced. A thorough and complete discussion of this topic would become so replete with equations and mathematical phraseology that only a specialist in the field would be equipped to handle it. It is the aim of this monograph to present a readable account of crystal analysis including such pictures and mathematical equations as make for clearness and interest and to omit highly technical data.

A BRIEF HISTORICAL OUTLINE OF THE DEVELOPMENT OF EXISTING X-RAY DIFFRACTION METHODS

It is impossible to give a perfectly fair historical account of the growth of methods of diffraction analysis - "too large a part of progress in any field of science has its origin not only in the daily environment but in the chance contacts and discussions of those persons making it. The following then is merely an attempt to give a chronological statement of the process by which existing methods have become available."[1]

The idea that X-rays can be diffracted arose from the interaction between the very old theoretical view of a crystal as a regular and indefinitely extended arrangement of atoms or molecules and the prevailing hypothesis concerning the nature of X-rays themselves. For many years after their discovery, the fundamental character of X-rays was completely in doubt. By many they were supposed to be a corpuscular form of radiation like the electrons. Others thought that they were the irregular "ether" pulses called forth by electrons striking the target of an X-ray tube. Some considered them to be wave motions - longitudinal with great wave length, mixed longitudinal and transverse, transverse with very long wave lengths and transverse with very short wave lengths. In order to discriminate between these hypotheses various unsuccessful attempts were made to refract and to reflect X-rays. Further efforts to diffract X-rays through small apertures showed that if they were transverse wave motions analogous to ordinary light, as much of the existing evidence seemed to indicate, their wave lengths must be not appreciably greater than 10^{-9} cm. The knowledge of the number of atoms in the gram molecule of a substance had already shown

[1] R. W. G. Wyckof - Structure of Crystals, P. 222

that the mean distance apart of the neighboring atoms in a crystal is of the order of 10^{-8} cm. With this information at hand and at a time when active attempts were being made to explain various optical properties of a crystal from the standpoint of structure theory, Dr. M. Laue, a member of the staff of the University of Zurich, suggested that if X-rays are such short waves, the regular arrangement of atoms which constitutes a crystal ought to act toward them as a kind of three-dimensional diffraction grating. These ideas proved to be correct, for when the experiment of passing a pin hole beam of X-rays through a thin section of copper sulphate crystal was tried, the now familiar spot photograph or Laue photograph was obtained. When subsequent observations had shown that the type of diffraction pattern thus prepared was dependent upon the crystal used and conformed to its symmetry requirements, a way was opened for the investigation of the internal constitution of crystalline solids.

The subsequent development of orderly methods of structure determination from this fundamental experiment has arisen through the use of information of both a theoretical and an experimental character. Ever since it became customary to look upon a crystal as an assemblage of atoms a chief concern of theoretical crystallographers has been the definition of all the atomic groupings which could have the symmetry of crystals. This problem appears to have found its final answer in the completion of the theory of space groups a little less than a decade before the discovery of X-rays.

The origins of this theory lie in the beginnings of crystallographic thought. It commenced to assume definite and precise form, however, with the work of Frankenheim and Bravais upon space lattices.

The lattices define merely the patterns according to which atomic groupings are repeated throughout the space. They all possess the complete symmetry of the system to which they belong and it was necessary to search for an explanation of tetartohedral and hemihedral properties in the arrangement of the atoms within these atomic groups. After the growth of the mathematical theory of groups had made it possible, such an extension of the symmetry requirements to atomic positions was made by Sohncke. In this way he succeeded in defining all of the space groupings of symmetry elements which would give rise to "molecules" having the same shape and a like orientation throughout a crystal. The theory of space groups thus begun was completed by the introduction of the concept of an enantiomorphic arrangement of the atomic groupings through the almost simultaneous efforts of E. Fedorov, A. Schoenphes and W. Barlow. To make them directly useful in determining the structure of crystals it has, however, been necessary not only to give the results of space group theory an analytical expression but to extend them to all possible atomic positions through the deduction of the special cases.[1]

The resulting ability to write down all possible atomic arrangements for acrystal would be of no practical importance if it were not at the same time possible to distinguish between them. It is the ability of X-ray diffraction effects to make these distinctions to a greater or less extent which has brought the subject of crystal structure study out of the realm of pure speculation into the field of experimentally determinable science.

Together with the observation showing the existence of the X-ray diffractions Laue presented a theory to account for them as arising from the interference of trains of X-ray waves scattered by the atoms of the

[1] Wyckoff - Structure of Crystals. Chapter I

diffracting crystal. Zinc blende (ZnS) was treated in this way upon the assumption that it was built up of molecules arranged upon a simple cubic lattice and that the X-ray beam consisted of rays of five different wave lengths. W. L. Bragg[1] showed that the data are more consistent with the hypothesis that the diffraction spots arose from the scattering of a beam of "white" X-rays by molecules having a face-centered[2] grouping in accordance with the demands of the now discredited valency-volume hypothesis of Barlow and Pope[3]; he further proposed that the phenomena are more easily described as reflections from the parallel planes of atoms within the crystal. This explanation implied that X-rays should be "reflected" from the faces and led to the development of the X-ray spectrometer.[4] Around this instrument has grown up the entire field of X-ray spectroscopy. At the same time the various crystal structures suggested with its aid have focused attention upon the usefulness of diffraction methods in experimental investigations of crystal structure.

An X-ray analysis of zinc blende and the accurate placing of the sulphur atoms in pyrite emphasized the larger amount of information that can now be obtained from Lane photographs. The essence of these studies underlies most subsequent work with Lane photographs.

From the experimental standpoint the third outstanding development has been the extension of diffraction methods to crystalline powders. It is natural that after diffraction effects had been produced with single

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[1] W. L. Bragg -Proceedings Cambridge Philosophical Society 17, I, 43 (1912)

[2] Arthur Haas - Atomic Theory, P. 69

[3] R.W.G. Wyckoff - Structure of Crystals, P. 224

[4] W. H. and W. L. Bragg - Proceedings Royal Society A, 88, 428 (1913)

crystals, attempts should be made to get them from all manner of substances. They were sought from powders, liquids, fibers, and substances in various other special states of aggregation. Though a sort of band was thus observed from a crystalline powder the use of heterochromatic X-rays made it impossible to obtain a clearly defined pattern. When later a tube operated to emit nearly monochromatic X-rays was employed, usable powder photographs became realities.[1]

A science of crystal structure determination began to arise when a meeting was effected between these experimental methods of diffraction study and the results of theoretical crystallography. At least two independent and only slightly related efforts to develop adequate methods of study have been made. One of these has arisen through contributions from several European works as Ewald, Gross, Niggli, Schiebold and Aminoff; the other had its origins in the early attempts of S. Nishikawa[2] to use space group results in studies of crystal structure.[3]

1 A. W. Hull - Physical Review, 10, 661 (1917)

2 S. Nishikawa - Proceedings Math. Phys. Soc. Tokyo, 8, 199 (1915)

3 R. W. G. Wyckoff - Structure of Crystals, P. 225

RÖNTGEN RAYS

When the motion of rapidly moving electrons is checked the resulting phenomena represent a reversal of the photo-electric effect. The kinetic energy of corpuscular radiation is then partially transformed into electromagnetic wave energy; and the arrest of a rapid motion of electrons thus produces the remarkable rays discovered by Röntgen in 1895, and known as Röntgen rays or X-rays.[1] X-radiation is produced whenever fast-moving electrons impinge upon matter. An X-ray tube is essentially a device for making possible this interaction. In its first forms it consisted of a glass tube with two metal electrodes between which a high voltage direct current could be passed. When the pressure in such a tube is reduced to a fraction of a millimeter electrons will be projected from the cathode and will give rise to X-rays on striking the metallic face of a target or anticathode interposed in their path. These early "gas tubes" were troublesome to operate because the character of the X-rays which they emit is conditioned in part by the pressure of the gas remaining in the tube and because this pressure itself changes as the tube is operated. Since 1913 the X-ray tube invented by Dr. W. D. Coolidge, Assistant Director of the General Electric Research Laboratory at Schenectady, N.Y. has come into universal use.[2]

Figure 1 - A Coolidge X-Ray Tube

[1] Arthur Haas - Atomic Theory, P. 54

[2] Saunders - Survey of Physics, P. 588

In the Coolidge form the tube is highly evacuated and the electrons come from the heated filament F as thermions. Their number can be varied by changing the heating current sent through this filament. Their speed, however, depends on the high difference of potential separately maintained between F and A, the metallic target on which the electrons fall. The pressure in the tube is about a millionth of a millimeter of mercury.

The most striking property of Röntgen rays is their extraordinary power of penetration. They are scarcely absorbed at all by objects which are completely opaque to ordinary light. Among their other properties, particular mention should be made of their strong ionizing power, and the fact that they experience no deflection whatever either in a magnetic or in an electric field; it thus appeared that Röntgen rays could not be of a corpuscular nature. The penetrating power, or hardness, was soon found to be a reliable characteristic for distinguishing between various kinds of Röntgen rays; the greater or smaller the power of penetration, the harder or softer is the relevant radiation said to be.

The nature of X-rays was in doubt for many years after their discovery. The observation of their diffraction by crystals and the successful interpretation of these effects in terms of the arrangements of the atoms in crystals has, however, shown unmistakably the fundamental similarity between X-rays and ordinary light radiations.

TYPES OF SPACE LATTICES
THEIR IDENTIFICATION BY MEANS OF X-RAY SPECTRA

Since crystals are composed of regularly distributed atoms which can act as scattering centers, diffraction effects may be expected from their interaction with X-rays having wave lengths comparable with the inter atomic distances. The nature of these effects depends upon the kinds and positions of the atoms in a crystal; consequently, the theory which describes them in terms of atomic positions forms the basis of studies of crystal structure using X-rays.

A complete theory would develop in detailed expressions to describe the diffraction patterns resulting from any conceivable arrangement of atoms. The solution of the problem in this general form is accompanied by analytical complexities which add little to an understanding of the requisite physical assumptions. For this reason an approximate treatment of only the mathematically simplest case of cubic crystals is outlined here.[1]

Diffraction effects are characterized by both position and intensity. The first of these can be completely and exactly predicted but at the present time even relative intensities can only be approximately foretold.

In order to understand the behaviour of crystals with respect to Röntgen rays, we shall first consider, as the simplest of all gratings or lattices, a line-lattice in which the lattice points are arranged at equal intervals along a straight line. The constant interval between two successive lattice points is called the lattice constant.

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[1] R. W. G. Wyckoff - Structure of Crystals, P. 89

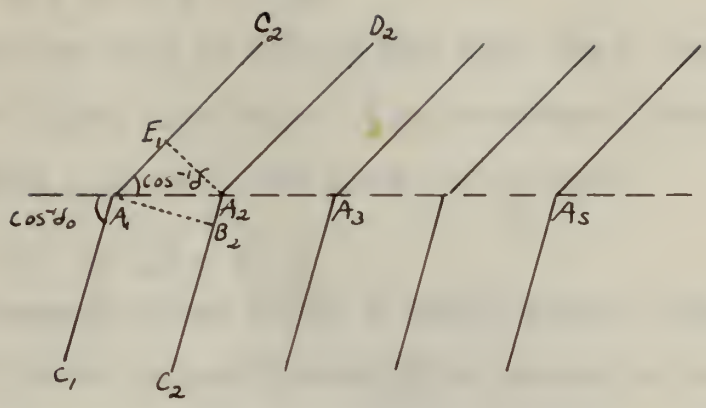

Figure 2 - Simple Line Grating [1]

The points of the row A_1, A_2, A_3 . . A_s of Figure 2 are separated by the constant interval A_1A_2 A_2A_3 C. It will be assumed that these points can act as diffracting centers for any chosen parallel beam of rays such as C_1 D_1. The difference in path, and consequently the retardation of the ray C_1C_2, diffracted by A_1, compared with the ray D_1D_2 is $e(\delta-\delta_0)$, where the direction cosine of the incident beam with respect to the row A_1 . . . A_s is

$$\delta_0 = \cos \angle A_1 A_2 D_1 = A_2 B_2 / e$$

and that of the diffracted ray is

$$\delta = \cos \angle C_2 A_1 A_2 = A_1 E_1 / e$$

If this path difference is equal to their wave length, or some integral multiple thereof, reinforcement will take place between the two rays; otherwise with an extended row of diffracting centers there will always be destructive interference between neighboring points if the waves are exactly out of phase, or between more distant atoms for some other phase difference.

[1] R. W. G. Wyckoff - Structure of Crystals, P. 90

If λ is the wave length of the diffracted waves and h_o' is some integer, then constructive intereference will be observed when

$$e(\delta - \delta_o) = h_o' \lambda$$

This is essentially the state of affairs that holds for a simple line grating. Rays of a given wave length λ are therefore diffracted only in those directions with a cosine $^{-1}\delta$ for which the relation

(1) $$e(\delta - \delta_o) = h_o' \lambda$$

is satisfied for integral values of the so-called ordinal number or order h_o'. Conversely, if the incident radiation is composed of rays of all wave lengths, it is resolved into spectra by the diffraction, a different diffraction spectrum corresponding to each value of the ordinal number h_o'.

It follows from equation (1) that diffraction can never occur unless $e > \lambda$

Moreover, e must not be much larger than λ, because otherwise, in the spectra of low order which are of particular importance, the difference $(\delta - \delta_o)$ would be too small and the spectral resolution insufficient. In the best optical line gratings as the Rowland concave gratings, e is always less than ten times the wave length.[1]

In a crystal that is diffracting X-rays the atoms, as diffracting centers, are arranged regularly in three dimensions. If these atoms lie at the corners of unit cells of a cubic crystal, that is, at the points of a simple cubic lattice - the conditions for reinforcement of the diffracted rays will be similar to those for a single row of points.

[1] Haas - Atomic Theory, P. 60

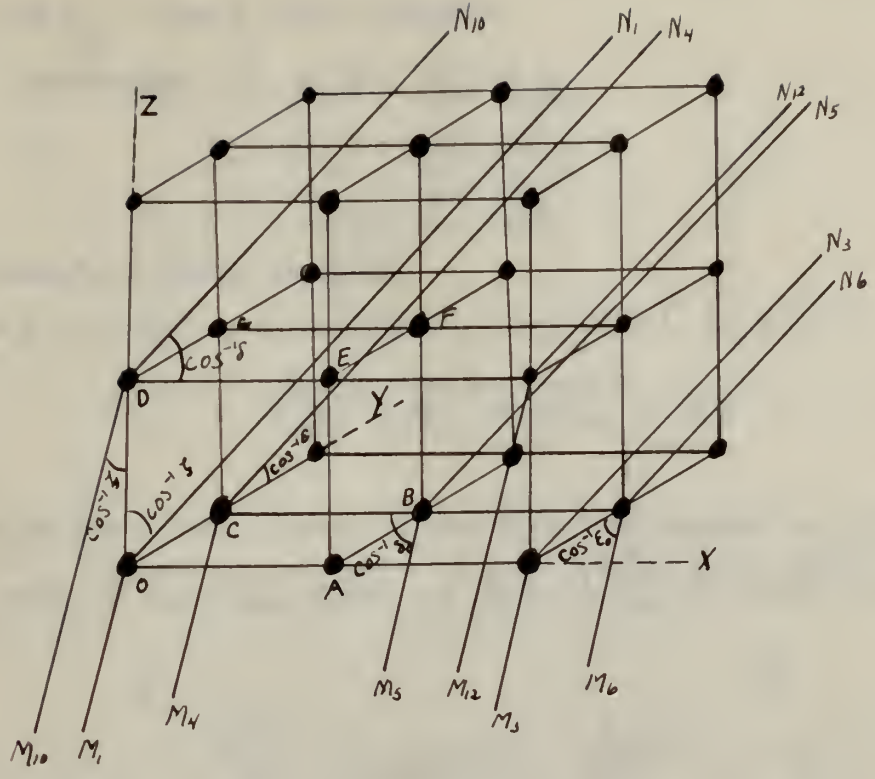

Figure 3 [1] (The diffraction relations of the rays $M_p N_p$ for a simple cubic arrangement of diffracting centers. The cube OABCDEFG is the unit)

In this simple case Figure 3, δ_0, ε_0 and ζ are the direction cosines of the incident ray and δ, ε, ζ are the corresponding ones for the diffracted beam, all measured with relation to right angled cartesian coordinates, the conditions for constructive interference of the rays $M_p N_p$ are determined by the three equations

$$a_0(\delta - \delta_0) = h_0' \lambda$$
$$a_0(\varepsilon - \varepsilon_0) = k_0' \lambda$$
$$a_0(\zeta - \zeta_0) = l_0' \lambda$$

[1] R. W. G. Wyckoff - Structure of Crystals, P. 91

where K_o' and l_o', like h_o' are integers.

Transposing
$$(\delta - \delta_o) = h_o' \lambda / a_o$$
(2)
$$(\varepsilon - \varepsilon_o) = k_o' \lambda / a_o$$
$$(\zeta - \zeta_o) = l_o' \lambda / a_o$$

Squaring these and adding together

$$\delta^2 - 2\delta\delta_o + \delta_o^2 + \varepsilon^2 - 2\varepsilon\varepsilon_o + \varepsilon_o^2 + \zeta^2 - 2\zeta\zeta_o + \zeta_o^2$$
$$= \lambda^2/a_o^2 (h_o'^2 + k_o'^2 + l_o'^2)$$

But since the sum of the squares of the direction cosines of a line is equal to unity $2 - 2(\delta\delta_o + \varepsilon\varepsilon_o + \zeta\zeta_o) = \lambda^2/a_o^2 (h_o'^2 + k_o'^2 + l_o'^2)$

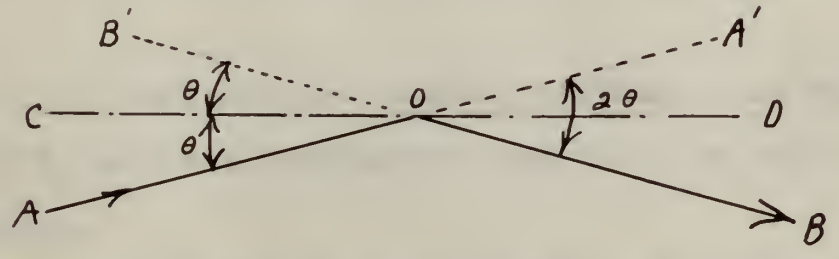

Figure 4[1] (If AO is an incident and OB a diffracted beam, $A^1OB = 2\theta$ is the angle of deviation and CD is the trace of the "reflecting" plane)

5 The angle of deviation 2θ, that is, the angle between the incident and the diffracted ray (Figure 4) is given by the usual relation

$$\cos 2\theta = \delta\delta_o + \varepsilon\varepsilon_o + \zeta\zeta_o$$

so that

$$2 - 2\cos 2\theta = \lambda^2/a_o^2 (h_o'^2 + k_o'^2 + l_o'^2) = 4\sin^2\theta$$

or

$$\lambda = 2a_o / \sqrt{h_o'^2 + k_o'^2 + l_o'^2} \sin\theta$$

[1] R. W. G. Wyckoff - Structure of Crystals, P. 92

If $h_o' = nh_o$, $k_o' = nk_o$ and $l_o' = nl_o$ where n is the highest common divisor of h_o', k_o' and l_o', then

$$3(a) \qquad n\lambda = 2a_o / \sqrt{h_o^2 + k_o^2 + l_o^2} \sin\theta$$

If the analogous expression is deduced for groupings of unit cells which possess other than cubic symmetry, they are found to have a corresponding form:

$$3(b) \qquad n\lambda = 2a_o / \sqrt{F(h_o, k_o, l_o; abc; \alpha\beta\gamma)} \sin\theta$$

where $F(h_o, k_o, l_o; abc; \alpha\beta\gamma)$ is a quantity involving second degree terms, in h_o, k_o and l_o and the crystallographic constants - the axial ratio and axial angles.[1]

A possible geometrical interpretation of the equation, particularly of the terms involving the integers h_o, k_o and l_o is suggested by the following considerations. As an ideal case are to be imagined two, or more infinitely thin sheets of plane transparent material parallel to one another and separated by a distance d

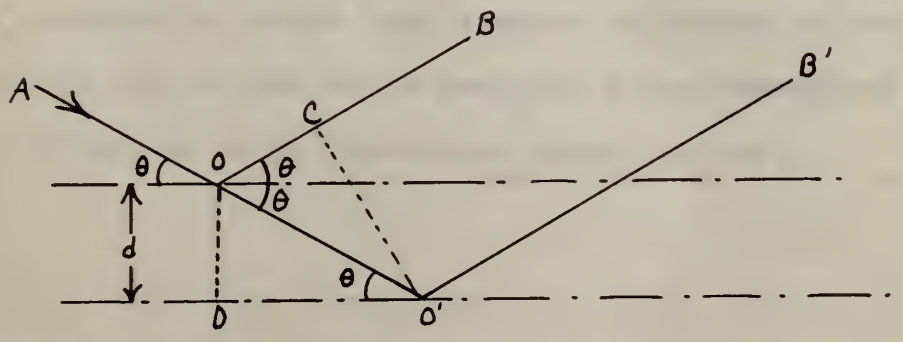

Figure 5 (The phase relationships of reflections from a pile of infinitely thin reflecting plates.)

[1] R. W. G. Wyckoff - Structure of Crystals, P. 92

If a beam of light AO strikes the sheets at the angle θ, some will be reflected along the line OB. Of the remainder, some will be reflected along O'B', the rest being transmitted at O' and this process repeated for other sheets which may be present. The difference in path between the ray AOB and the ray AO'B' is

$$Oo' - OC = \frac{d}{\sin\theta} - \frac{d\cos 2\theta}{\sin\theta} = \frac{d}{\sin\theta}(1-\cos 2\theta) = 2d\sin\theta$$

When this path difference equals half of one wave length, or some odd integral multiple thereof, the two beams AOB and AO'B' will be exactly out of phase and capable of destructive interference. When $2d\sin\theta$ is some number of whole wave lengths then the two beams will reinforce each other. Between these two extremes there will be a partial interference of the rays. Thus the light reflected from the two sheets of material will range in intensity continuously between zero and a maximum. If the number of sheets is increased, the interference would always remain constructive for the maxima and completely destructive for the minimal positions of half wave length differences in phase, but for the intermediate region the destructive interference will become more and more complete the greater the number of the sheets until eventually the reflection pattern will consist merely of a succession of bright beams separated by regions of total darkness. That this will be true may be seen from a consideration of the intensity of reflection in the simple case shown in Figure 6.

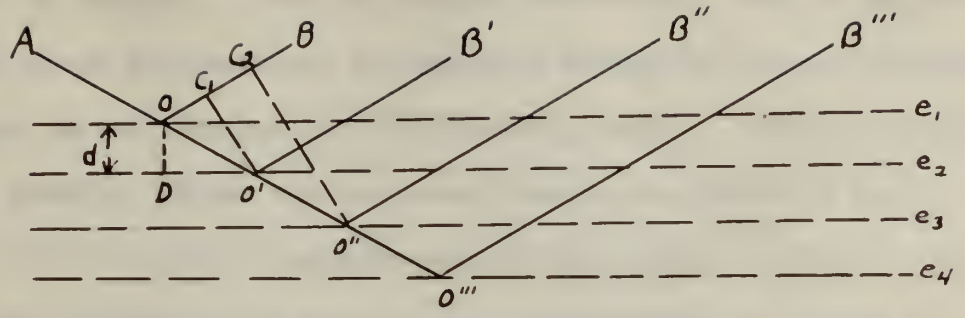

Figure 6 (In this figure the path differences)

$$A\,O'B' - AOB = OO' - OC_1 = \tfrac{1}{4}\lambda$$

$$AO''B'' - AOB = OO'' - OC_2 = 2OO' - 2\,OC_1 = 2\,(OO' - OC_1) = \tfrac{1}{2}\lambda$$

It is assumed in this figure that the path difference of the rays reflected by the first two sheets is a quarter of a wave length. With only two sheets in the pile the reflected beam would have a medium intensity resulting from the compounding of the two rays one-fourth a wave apart. If a third reflecting plate is added, its reflected ray AO"B" will be exactly opposite in phase to AOB and the resulting reflection will be diminished through a destruction of an amount of AOB equivalent to the amplitude of AO"B"; it will be still further lessened by the addition of a fourth sheet which will reflect AO"B" exactly out of phase withAO'B'. By the same procedure it is clear that as more plates are added the destructive interference will become increasingly effective and thus the intensity of reflection will approach closer and closer to zero. With enough plates in the pile, the same destructive interference obviously would take place with any fractional path difference between AOB and AO'B'. Consequently the intensity maxima from such a large pile of plates have

positions defined by the expression

$$n\lambda = 2d \sin\theta \qquad (3c)$$

where n is an integer. This expression has the same form as the equation (3a) which gives the positions of intensity maxima for X-rays diffracted by a simple cubic distribution of diffracting points. Since an infinite number of parallel planes can be passed through the points of such a grouping, this similarity suggests that it might prove convenient to consider the diffraction of such a regular arrangement of points as geometrically equivalent to reflection in a series of equidistant parallel planes. That diffracting points will send back a beam of X-rays incident upon it which would obey the law of ordinary reflection is seen from the usual Huygens construction.

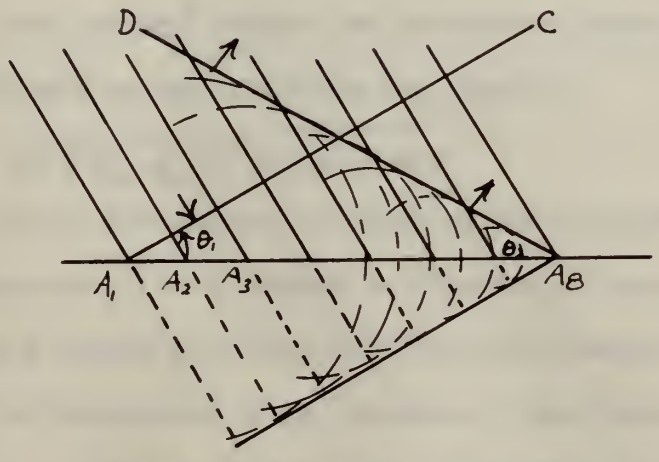

Figure 7 (Huygens construction to show that a wave front A_1C will be "reflected" as OA_8 by the regularly spaced diffracting points $A_1 - A_p$)

In Figure 7 if A_1C is the wave front of a beam incident upon a row of points $A_1, A_2, A_3 \ldots A_p$ capable of acting as diffracting centers it is immediately seen that a reflected ray will have the wave front A_8O

so situated that the angle θ, is equal to the angle θ_2. Hence, a set of lattice planes singles out from the incident radiation those rays for which an integral multiple of the wave length is equal to the difference in path between two rays, which are reflected from two successive lattice planes.

If the diffraction of the rays takes place in such a way that they appear to be reflected at the lattice planes in accordance with the usual law of optics, then the reflected rays must strengthen and weaken each other owing to interference.

As was shown before a space lattice only diffracts incident rays of quite definite wave length from radiation with a given direction of incidence. Thus complete diffraction of a narrow bundle of parallel rays can only be attained if the space lattice be rotated. A complete resolution into spectra is then actually attainable.[1]

Taking the analogy[2] between the reflecting sheets and the diffraction of X-rays by space lattice the quantity

$$a_0 / \sqrt{F(h_0, k_0, l_0, a\,b\,c, \alpha\,\beta\,\gamma}$$

of equation 3b can be interpreted in terms of the distance between planes of diffracting points. In a regular latticework of points it is always possible to pass a series of planes which will be parallel to one another and contain all of the points of the lattice. The planes of such a series will be separated by a constant interval and, having integral indices, will be parallel to some possible face of an analogous crystal.

The distance between two neighboring planes of such a series, Figure 8 can be calculated.[3]

[1] Haas - Atomic Theory, P. 65
[2] W. T. Bragg - Proc. Camb. Phil. Soc., 17, 43 (1913)
[3] A. W. Hull - Phys. Rev. 10, 661, (1917)

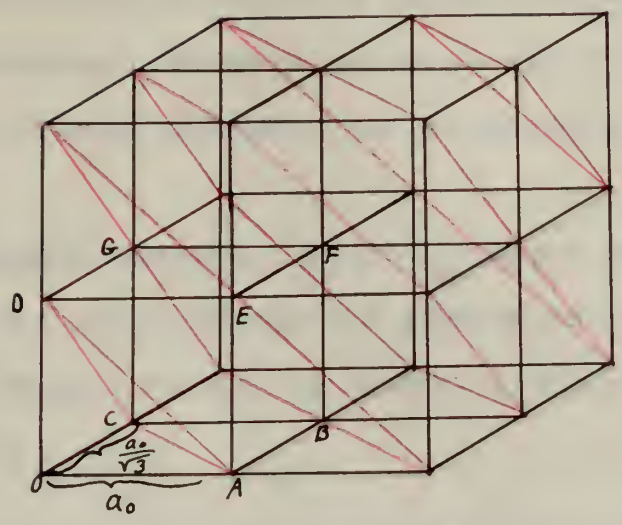

Figure 8 (The succession of (111) planes in a simple cubic arrangement of points. The cube OABCDEFGH is the unit)

From the identity in form between the expressions (a) for the diffraction of X-rays by regularly arranged diffracting centers in space and (b) for the reflection by uniformly spaced planes of diffracting centers the fundamental likeness of these two geometrical ways of receiving X-ray diffraction phenomena is established. The outstanding value of the reflection point of view probably lies in its ability to attach a readily pictured and usable significance to the phase numbers h_o, k_o, l_o of equation 3. This usefulness is particularly great in the treatment of diffraction effects from definitely oriented crystals since it employs the same indices required to describe crystal setting. A widespread application has followed the development of the reflection idea but the fact that it is essentially an artifice should be realized. As a geometrical analogy it

may be correctly used, but as long as X-rays are treated as wave motions their diffraction effects must be imagined as actually arising from the mutual interference of rays diffracted by spacially distributed scattering centers. As a consequence any discussion which aims to reproduce the physical mechanism of X-ray diffraction can not proceed from the reflection standpoint.[1]

The diffraction numbers h_o, k_o and l_o and the indices of sets of reflecting planes (h k l) are the same for extended groupings composed of an association of the unit cells of the systems of symmetry. It is permissible to write

$$(5)\quad n\lambda = 2d_{hkl}\sin\theta_n = 2a_o/\sqrt{F(hkl);abc;\alpha\beta\gamma}\ \sin\theta_n$$

as the expression governing the possible positions of effects from assemblages of diffracting centers arranged at the corners of unit cells having crystallographic symmetry.

It has been shown that for groupings built up from unit cubes

$$(4a)\quad d_{hkl} = a_o/\sqrt{h^2+k^2+l^2}$$

$$(5)a\quad n\lambda = 2a_o/\sqrt{h^2+k^2+l^2}\ \sin\theta_n$$

[1] R. W. G. Wyckoff - The Structure of Crystals, P. 97

Equations for the tetragonal, orthorhombic, hexagonal, rhombohedral, monoclinic, and triclinic unit cells have been set up.[1] Since one of the seven types of unit cells is fundamental to every possible crystal, equation (4a) gives the separation between geometrically like planes within any crystal. A knowledge of equations (4) and (5) solves completely the problem of the positions of diffraction effects from any space assemblage of diffracting points which possesses crystallographic symmetry. With their aid the angle through which X-rays incident from any direction upon a crystal will be bent can be predicted as long as the atoms, or other diffracting centers, can be considered to be regularly arranged in space in conformity with the crystalline symmetry. These equations indicate that the positions of X-ray diffractions are in no way dependent upon the particular manner of distribution of the atoms within a crystal but only upon the crystallographic characteristics (the axial angles and the axial ratio) and the absolute dimensions of the unit cell. If all cubic crystals which have unit cells of the same size, no matter what their chemical compositions and atomic or electronic distributions may be, they will give diffraction effects in identically the same positions. The same would be true of two crystals of any other symmetry which had unit cells of equal size and shape.

[1] Wyckoff - Structure of Crystals, P. 98

Intensity of X-ray Diffraction Effects from Crystals

Problems of atomic arrangement in crystals therefore must concern themselves with the other characteristic of diffraction effects - their intensities. From the standpoint of these problems intensity relations, either absolute or relative, cannot now be evaluated with even an approach to the completeness which marks the ability to predict diffraction positions. "Wave length data now call for 7 place logarithms but intensities have not yet graduated from the slide-rule class."[1] From the present stage of knowledge intensity relations can be best expressed by using the reflection analogy.

The difficulties of the problem are both experimental and theoretical. Complications arise when accurate intensity measurements are wanted. Several efforts[2] have been made to obtain theoretically sound intensity expressions but do not accord with experimental data without introducing empirical factors.

Intensity problems introduce two empirical factors[3]; one describing the dependence of intensity upon the scattering atoms, and the other expressing its variation with the angle of deviation. By assuming that the amplitude of X-rays scattered by heavy atoms in producing regular diffraction effects is greater than that of lighter atoms by an amount roughly proportional to the atomic number it is possible to deduce the structure of the simple crystals like the alkali halides. The study of the intensity of reflection from planes in these crystals shows in a general way how the intensity of reflection varies with the angle of deviation and also to what extent a proportionality between amplitude and atomic number is fulfilled. Since intensity of reflection is related to the internal structure of the

[1] D. F. Webster - Science 79, 194 (1934)
[2] C. G. Darwin - Phil. Mag. 27, 315, 675 (1914)
[3] W. F. Bragg - Proc. Roy. Soc. A 89, 468 (1914)

scattering atoms that quantitatively applicable laws can be found is doubtful. Working rules, however, that are approximately fulfilled for moderate angles of reflection may be used in the determination of crystal structure.

From earlier knowledge and with crystal structure data it is assumed that scattering power follows approximately the number of the scattering atoms. Existing information suggests that the amount of X-rays of ordinary wave lengths scattered by an atom will depend upon both the number and the positions of the electrons surrounding its nucleus. Since the number of electrons is comparable with the atomic numbers of the elements it is to be expected that the scattering power of an atom for such X-rays will be greater for heavy than for light atoms. The amount of radiation scattered by an atom will depend upon the interference which occurs between rays sent out by its electrons and this in turn will be a function of its electronic configuration. If the distance between these electrons were small compared with the wave length of the scattered X-rays, their intra-atomic interference would be negligible and there would be a linear proportionality between scattering power and atomic number. Many crystal data show that the heavier elements scatter appreciably more electron for electron than do atoms of low atomic weight so nothing more than a qualitative application can be given the proportionality between amplitude and atomic number. It is suggested by some to limit intensity comparisons to planes composed of only one kind of atom.

It has been seen that when the atoms are located only at the corners of unit prisms, the atomic diffracting centers in a crystalline structure will lie in a series of equally spaced planes parallel to any possible crystal face (h k l). The intensity of X-ray reflection from (h k l) in such a simple atomic grouping and in more involved ones after

They have been corrected for their more complicated structures, has been found to fall off rapidly with increase in the angle of reflection, or what amounts to the same thing, decrease in the spacing of like planes.

One of the known factors entering into the decrease in intensity with increase in the angle of reflection is the thermal agitation of the atoms about equilibrium positions, this ratio being known as the "normal decline." If this ratio is corrected as well as possible for the temperature effect and for the polarization factor the intensity of reflection appears to be roughly proportional to the square[1] of the spacing between like reflecting planes, that is $(d\ h\ k\ l/n)^2$. The "normal decline" is approximately given by $(d_{hkl}/n)^{2.35}$. There are many insufficiencies of the "normal decline" but in spite of this the structures of many crystals can be deduced with considerable certainty.

From this line of reasoning the best possible calculated approach to the observed intensity of reflection from a plane (h k l) of a simple unit cell array of atoms is given by

$$(6) \qquad I \propto \left(\frac{d_{hkl}}{n}\right)^2 \left(1 + \frac{\cos^2 2\theta}{2}\right) \sigma^2 = \left(\frac{d_{hkl}}{n}\right)^{2.35} \sigma^2$$

Where σ is the scattering power of the atoms making up the equidistant sets of planes parallel to (h k l) and o is a term expressing the effects due to thermal agitation.

In some powder photographs reflections have been obtained through angles for which $2\theta \quad 90^\circ$. These large angle reflections seem to show that as 2θ- approaches 180° the intensity of the diffraction effects increases again with the angle. To agree with this condition

$$7 \qquad I \propto \frac{H \cos^2 2\theta}{\sin^2\theta \cos\theta} \sigma^2 = \frac{1 + \cos^2 2\theta}{\cos\theta} \left(\frac{d_{hkl}}{n}\right)^2 \sigma^2$$

[1] W. H. Bragg - Phil. Mag. 27, 881 (1914)

For reflection angles θ greater than 45° this seems to be better than Eq. 6 but like all intensity expressions is empirical. Since most of the best data for crystal structure investigations involve angles 2θ less than a right angle Equation 6 seems to be the better form to use.

Another factor which can not be exactly evaluated and will enter these proportionalities is absorption. The influence of absorption probably depends upon the degree of perfection of the crystal. Experimenters allow for these discrepancies while performing the experiment and feel their results are fairly accurate.

The intensity of reflection will also depend upon a phase or structure factor. A cubic lattice may be simple, space-centered or finally, face-centered. The symmetry relations are the same in all three cases but each has its own particular properties. A cubic lattice is spaced-centered when, in all the elementary cubes whose edges are given by the lattice constant, an additional lattice point is situated at the center of the cube; each elementary cube then contains nine instead of eight lattice points. If, however, the interior of the cube is unoccupied, while lattice points are situated at the centers of the six faces, a face-centered lattice results. After considering each type, an expression, namely

$$8 \quad I \propto \left(\frac{d_{hkl}}{n}\right)^{2.35} \times (A^2 + B^2) \quad (1)$$

has been developed which will give the relative intensity of reflection from any plane of any distribution of atoms in a crystalline structure

With Equations 5 and 8, certain definite statements which are the chief postulates of X-ray diffraction phenomena for crystal structure determination can be made.

[1] R. W. G. Wyckoff - Am. J. Sci. 50, 317 (1920)

These are:[1]

(1) "X-rays behave as if they are light waves of short wave length which can be diffracted by the atoms in crystals. The approximate length of these waves can be obtained by application of quantum principles.

(2) "The two 'laws' of scattering are approximately, but only approximately, fulfilled. The first of these states that scattering power follows roughly the number of electrons in an atom; according to the second the intensity of diffraction falls off with increased angles of diffraction, at least until 2θ in the preceding equations reaches a right angle. As a working expression of these 'laws' it is considered that the requirements of expression (6) must be qualitatively met; the lack of precise knowledge of scattering, however, makes it impossible to set definite limits to their permissible variation. The element of personal judgment which must often be introduced makes this postulate the most unsatisfactory of those which must be used.

(3) "The use of the theory of space groups in crystal analysis permits the search not only for a possible structure but for the only one possible in the light of the two preceding postulates concerning the properties of X-rays. To achieve such unique solutions through the application of space group theory it is assumed (1) that the atoms giving observable diffraction effects occupy equilibrium positions fixed by the symmetry of the crystal and (2) that the results of the theory of space groups define all of the equilibrium atomic positions possible for any crystal."[1]

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1 R. W. G. Wyckoff - The Structure of Crystals, P. 107

Laue Photographs

If crystals possess the structure of space-lattices and their lattice constants, though larger, are not much larger than the wave-lengths of Röntgen rays, these rays should be diffracted by interference within the crystals. An experimental proof of an interference of X-rays produced by crystals would therefore, on the one hand, demonstrate the lattice structure of crystals, and, on the other hand, confirm the conjecture that X-rays are electromagnetic waves with a wave-length of the order of 10^{-9} cm.

Starting out with this idea, Laue, in 1912, was the first to investigate the action of crystals on X-rays, and actually to demonstrate experimentally the suspected phenomena. In these researches Laue worked in collaboration with Friedrich and Knipping[1].

Laue photographs of a substance which forms good crystals are easily made.

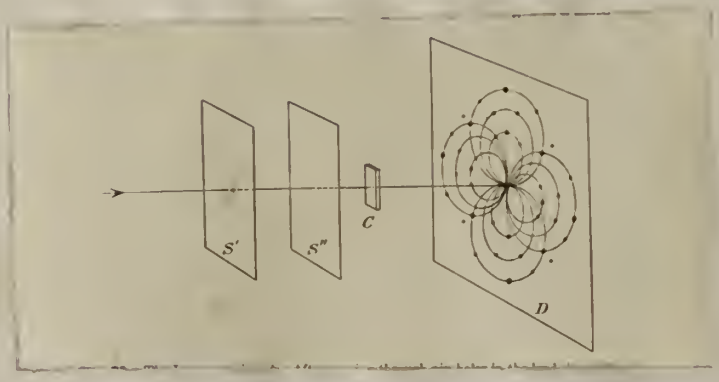

Figure 9 - The Laue Experiment

[1] Hass - Atomic Theory, P. 68

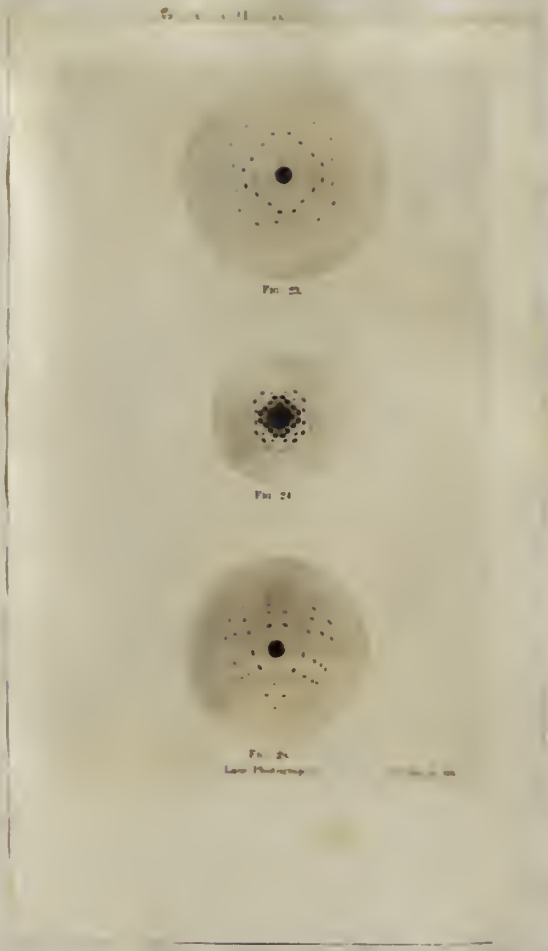

Figure 12 - Laue Photographs

A fine X-ray beam, defined by passage through pin-holes in two, or more, sheets of lead s' and s" will be diffracted by a thin section of crystal of c. The resulting slit images arranged in a more or less symmetrical fashion about the undeviated central image upon a photographic plate ( ) constitute a Laue photograph. The symmetry of distribution of these spots is related to that of the crystal giving use to them. Experiment actually gave the results as predicted by the formula set up to determine these positions of the spots.

In Figures 10 and 11 are reproduced Laue photographs which were obtained with a crystal of zinc blende (ZnS). In the exposure shown in Figure 10, the distance of the plate from the crystal amounted to 3.5 cm., whereas it was only 1 cm. in the exposure reproduced in Figure 11. The effect of variations in distance upon the size of the resulting Laue patterns is illustrated by these photographs.

In both exposures, the rays met a face of the cube at right angles. Their direction was therefore that of an edge of the cube, and this explains the "fourfold symmetry" to be observed in the photographs. An axis of symmetry in a crystal is termed "n" - fold, when through this axis n planes can be drawn, with respect to which the crystal is symmetrical. In a regular crystal each edge of a cube represents a fourfold axis of symmetry for through each edge four planes of symmetry can be drawn, the lines along which they intersect a plane normal to the edge being represented in Figure 13; two of these intersecting lines are again edges, and two face diagonals.

Figure 13 - Fourfold Symmetry

The photographs exhibit a fourfold symmetry, provided that the incident pencil of rays be perpendicular to a face of the cube. Corresponding to Fig. 13, four lines of symmetry are to be recognized, and hence all spots provided they do not lie just on a line of symmetry are repeated eight times in all. This can be seen in Figs. 10 and 11.

If the ray falls perpendicular on an octohedral face cut from a regular crystal, geometrical considerations show that its direction is that of a trigonal axis of the cube - a threefold axis of symmetry. An exposure made in this way is reproduced in Fig. 12 in which each spot occurs six times.

Dimensions for Laue photographic apparatus can be seen by referring to Fig. 9. The lead slits S' and S" may be from eight to ten centimeters apart and 1/8 inch thick with pin-holes approximately 1.2 millimeters in diameter. The crystal section should if possible have an area large enough to cover the bundles of X-rays proceeding from the pin-holes. This, however, is not necessary: photographs suitable for crystal structure determinations have been prepared from crystals with a maximum dimension less than one millimeter. The thickness of the crystal will be anywhere from about one tenth of a millimeter to one millimeter. The specimen should be thinner, the higher the density and consequently the greater the absorbing power of the crystal for X-rays. If both the diffracting and the absorbing powers were adequately known, it would be possible to calculate an optimum thickness for any crystal. The crystal may be either pasted directly over the last lead slit or mounted upon some form of crystal holder. The first procedure is the simpler, the second has the advantage of allowing the crystal to be so mounted that both its orientation with

respect to the X-ray beam and changes in this orientation for the preparation of additional photographs can be more precisely stated. Since the spots characteristic of Laue photographs are produced by X-ray beams proceeding from the illuminated crystal, the size of the Laue pattern will be proportional to the distance from the crystal to the photographic plate. For cubic crystals and others having an axial ratio not too greatly different from unity, this distance may conveniently be made equal to five centimeters. With other crystals a plate distance of four and sometimes three centimeters is found useful. The effect of variation in this distance upon the size of the photographs can be seen in Figs. 10 and 11.

The X-rays which produce Laue spots lie in the region of white or general radiation. The most useful Laue photographs for the determination of the structures of crystals are prepared with a maximum tube potential of 50 to 60 kilovolts. Of the commercially available X-ray tubes one with a tungsten target is most satisfactory because it gives the greatest amount of continuous radiation. At this voltage an exposure of 15 milliampere-hours is usually sufficient to produce good Laue photographs. The length of exposure depends somewhat upon the thickness and size of the crystal specimen and largely upon its absorbing power. Laue photographs which exhibit a very large number of spots can be produced by operating the tube at a voltage higher than 60 kilovolts not only because the efficiency of production of white X-rays increases with increased voltage but also because many more atomic planes are in a position to reflect the shorter X-rays thus produced. High voltage Laue photographs are good when only symmetry information is wanted.

The grave injuries to the health of the experimenter which result from exposure to X-rays require that care be taken in the shielding of

X-ray tubes during the preparation of diffraction photographs. This protection must be even more effective than that employed in ordinary medical use of X-rays, because of the long exposures required in obtaining crystalline diffraction. Small leaks which would be negligible over a period of a few seconds may become of great importance after several hours. For these reasons all X-ray tubes used in crystal analysis should be enclosed in boxes covered with a thickness of lead sufficient to prevent the deterioration after several months of exposure of photographic plates placed outside the boxes.

An improved form of apparatus for the production of Laue photographs is shown in Fig. 14.[1] Its essential parts are mounted upon a brass base.

Figure 14 (An Improved Form of Apparatus for the Production of Laue Photographs)

[1] Wyckoff - The Structure of Crystals, P. 115, Fig. 81

The crystal specimen held on a microscope slide is mounted in a crystal holder (c) and centered with the aid of the removable template shown at G. The motions of the crystal at right angles is measured by c_1 and c_2 while the collar H supporting the crystal can be rotated. This last motion is of particular advantage with strongly absorbing crystals because a series of unsymmetrical Laue photographs in slightly different orientations can be prepared by thus turning the crystal without largely altering the absorption in different parts of the photographs.

If the length of the side of the unit cell has been determined by some other procedure, then the wave lengths of the several hundred reflections found upon an ordinary Laue photograph can be calculated. Among these there will be a considerable number which are produced by X-rays for which $n\lambda$ lies between λ min and 2λ min, and which consequently provide a large mass of data available for use in crystal analysis. An outstanding advantage of the Laue photographs for this purpose arises from the fact that it is possible with these many reflections from planes with complicated indices to make intensity comparisons between planes of different forms to which the same kinds of atoms contribute but which still have the same or closely similar spacings. Thus the uncertainties concerning the laws governing the scattering of X-rays are eliminated as far as possible.[1]

If the length of side of the unit cell is not found by another procedure it could still be approximately determined from a use of the short wave length limit, λ min, as calculated from the impressed voltage. In practice this is unnecessary because whenever a Laue photograph can be prepared a spectrometer measurement is possible. The knowledge of λ min. is useful however in deciding between the different unit cells possible for other than cubic crystals.

[1] Wyckoff - The Structure of Crystals, P. 147 and 148

X-ray Spectrometry

In accordance with equation 5

$$n\lambda = 2d_{hkl} \sin \theta_n$$

a beam of X-rays A B Fig. 15[1]

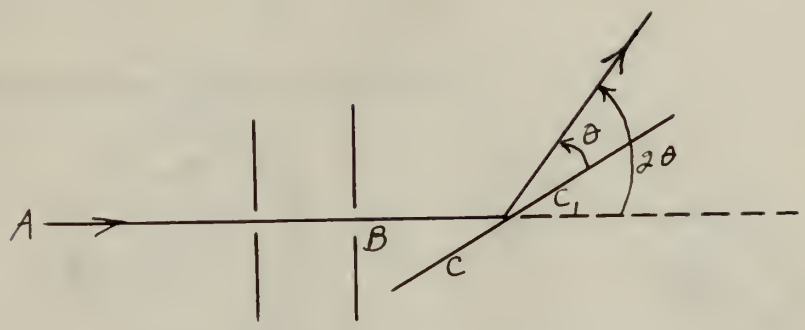

Figure 15 (Reflection of an Incident Beam on a Crystal)

incident upon a crystal face C C' will be reflected at certain angles, and at these angles only. An X-ray spectrometer is an instrument which determines the ratio $n\lambda / d_{hkl}$ by measuring the angle θ_n of reflection of the X-rays from individual crystal faces. If the wave lengths of the rays are known, this ratio will give the absolute distances between physically, but not necessarily geometrically, alike atomic planes in different crystals; or, if the same crystal face is employed, this ratio will measure the relative lengths of X-rays from different sources. Studies of atomic arrangement are concerned with only the first of these two uses.

The usual form of X-ray spectrometer Fig. 16[2] is the type developed by Bragg.

[1] Wyckoff - Structure of Crystals, P. 149

[2] W. H. Bragg and W. L. Bragg - X-Rays and Crystal Structure, P. 23

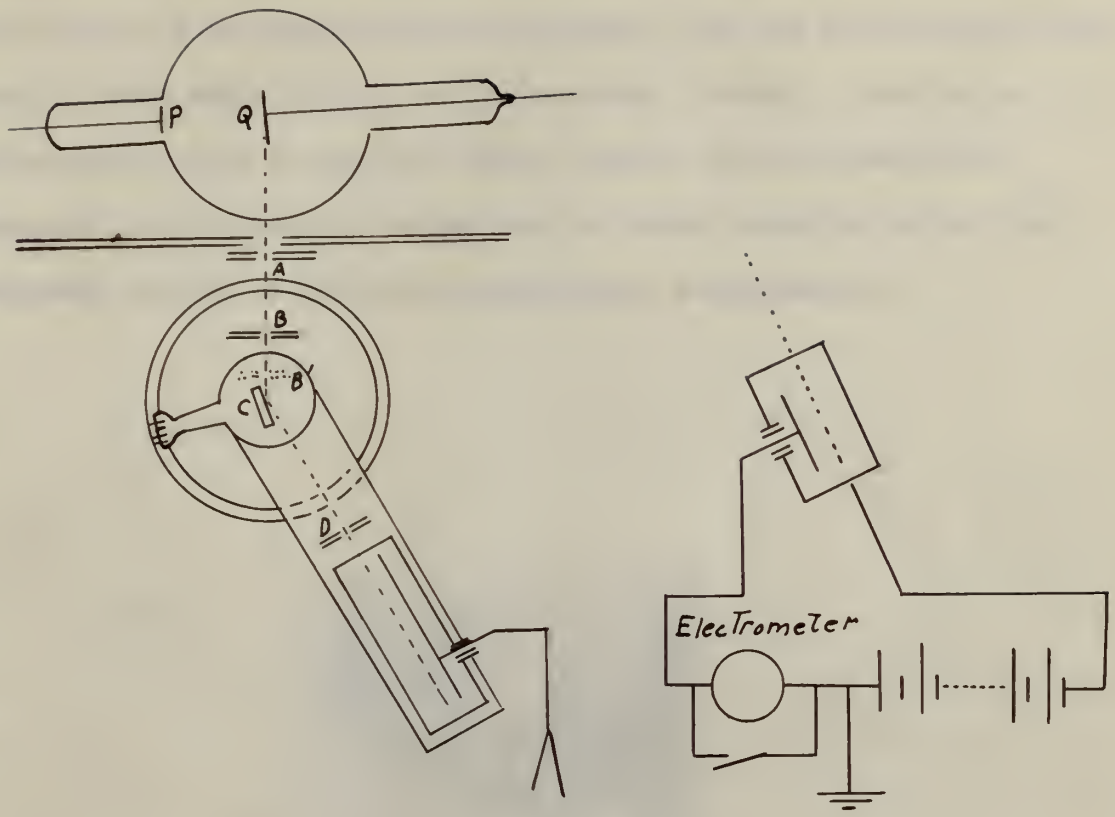

Figure 16[1] (X-Ray Spectrometer)
Figure 16a (Electrometer)

The X-ray bulb is enclosed in a wooden box coated with lead of 2 mm. thickness and with an additional shield of 5 mm. thickness on the side of the box next to the apparatus. The bulb is so mounted that it can be adjusted to an exact position. The slit at A permits a fine pencil of rays to issue from the box with B and B' to cut off stray radiation. The crystal C is mounted on a revolving table carrying an arm, at the end of which is a vernier working in conjunction with a graduated circle. The reflected pencil of X-rays pass into an ionization chamber mounted so as to be capable of revolving about the same vertical axis as the crystal table. The chamber is filled with a gas which absorbs the X-rays strongly

[1] Saunders - Survey of Physics, P. 589

and so yields a large ionization current. The chamber is insulated from the earth and raised to a high potential by a battery of storage cells. The electrode M is mounted in the cynlinder, just out of the way of the stream of rays which enters, and is connected through a mounting in a sulphur plug P with a fine wire which leads to an electroscope W. Figure 17[1] illustrates the arrangement of these essential parts in an instrument capable of furnishing approximate measurements.

Figure 17 (Rough Form of X-Ray Spectrometer)

1 Wyckoff - Structure of Crystals, P. 150

The distance of the second (S_2) of the two slits, S_1 and S_2 (of variable widths), from the crystal table C can be altered at will. The crystal specimen to be examined is mounted with wax upon a holder standing on the spectrometer table. This holder can be tilted to bring the plane of the slit beam of X-rays and of the correct crystal face into coincidence. If a large crystal is available the face from which the reflection is to be taken can be mounted in place with the aid of a removable templet. With a crystal too small to cover the entire X-ray beam it is often desirable to limit the exposed crystal surface with an opening of definite size. A variable diaphragm made for this purpose from platinum foil is shownat C. For many measurements it is more accurate to study the internal reflections obtained by passing the X-rays through a thin section of crystal rather than reflecting them from a developed face. The crystal holder should also be fitted with a pin or other device for locking it in a definite and reproducible position upon the table arm J; in this way the angular position of the crystal can be exactly defined by the vernier K reading upon the graduated circle G. Reflected X-rays pass through the defining slit S_3 of variable width into the ionization chamber (D) by a window covered with aluminum foil or mica. In the spectrometer of Fig. 17 the ionization chamber is a brass cylinder about 5.5 cm. in diameter and 16 cm. long. The internal electrode is a brass rod running longitudinally along the tube immediately out of the direct path of the entering rays and insulated from the case by a plug of sulphur. This electrode is connected with an electroscope E by a wire passing through the earthed shield H. A voltage of about 400 volts is impressed upon the case of the ionization chamber. The current which results from the ionization of the gas by entering X-rays flows between the charged case and the previously earthed electrode-

electroscope system. The consequent change in the potential of the latter, as read by the electroscope, measures the intensity of X-ray reflection. In making such an observation of intensity it is customary to break the earthing key after turning on the X-rays, and to observe the deflection of the leaf with a microscope and scale. Before spectrometric observations can be made it is necessary that the tube be warmed up until the source of X-rays no longer changes its position by expansion of the target. For this reason the tube is kept running continuously and a lead shutter to control the time during which the X-rays strike the crystal is used. The electroscope of Fig. 17 is of the "tilted" type. In general better results will be obtained by using a quadrant electrometer instead of an electroscope.

The ionization chamber should be prepared for use by passing the ionizing gas through it until most of the air has been displaced. At L_1 and L_2 are shown mercury traps that are useful for controlling the flow of this gas and reducing its subsequent loss.

A point of importance not only to X-ray spectrometry but also to X-ray spectrography is that if the distance from the crystal to the slit source is equal to the distance from the crystal to the indicating device, there will be a focusing of reflected X-rays of a definite wave length at the latter, even when the original beam is quite divergent.[1] In Fig. 18[2] O is the slit source and A is the

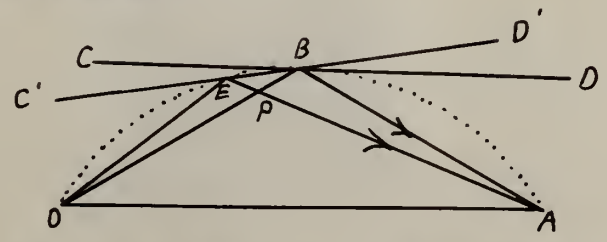

Figure 18 (Focusing of Reflected X-rays)

[1] W.H. and W.L. Bragg - X-Rays and Crystal Structure, P. 31

[2] R.W.G. Wyckoff - The Structure of Crystals, P. 152

ionization chamber slit S_3 of Fig. 17. The axis of rotation B of the of the crystal face is so placed that OB = BA. In the position CD of the face, the angle CBO = ∠DBA and the ray reflected by CD passed along the line BA

$$\Delta\ E\,O\,P \sim \Delta\ B\,P\,A$$

because $\angle E\,P\,O = \angle B\,P\,A$

and $\angle O\,E\,A = \angle O\,B\,A$

$$\therefore \frac{O\,P}{P\,A} = \frac{E\,P}{P\,B} \quad \therefore \Delta\ E\,P\,B \sim \Delta O\,P\,A$$

$$\angle B\,E\,P = \angle B\,O\,A$$

$$\angle B\,E\,P + \angle A\,E\,O + \angle O\,E\,C' = 180^{\circ}$$

$$= \angle A\,B\,O + \angle B\,A\,O + \angle B\,O\,A$$

$$= \angle A\,E\,O + \angle B\,A\,O + \angle B\,E\,P \quad \text{(from above)}$$

$$\therefore \angle O\,E\,C' = \angle B\,A\,O$$

Since $O\,B = B\,A$

then $\angle B\,O\,A = \angle B\,A\,O$

and $\angle D\,B\,A = \angle B\,E\,A = \angle C\,B\,O = \angle C'EO$

Thus the rays reflected by C D and C'D' at B and E both pass through A or X-rays of the wave length that passed along B A will travel along E A for the new crystal position and will be focused at A.

Spectrographic Methods

Spectrographic methods differ from those of spectrometry in the use of a photographic plate rather than an ionization chamber as an indicating device. A small portion of an X-ray spectrum can be photographed simply by employing a somewhat divergent beam and putting a photographic plate in the position of the chamber slit of a spectrometer. If the crystal is poorly constructed the spectrum may be badly distorted. Its definition will be greatly improved and at the same time a complete record of the reflections from all possible planes will be obtained by rotating the crystal during the exposure back and forth over a prescribed angular range.

A crude form of spectrograph is shown in Figure 19.[1] X-rays pass through the variable lead slits S_1 and S_2 and strike the reflecting crystal mounted upon a rotating crystal holder at C. It is customary in accurate spectrographic observations for crystal analysis to make a photograph from the crystal under investigation and one from a standard crystal usually calcite or rock salt on the same plate. The crystal holder consequently must consist of a table and a templet for mounting these two crystals in wax. Unless a very large extent of spectrum is to be

Figure 19 (A simple form of X-ray spectrograph for use in crystal analysis)

1
R.W.G. Wyckoff - The Structure of Crystals, P. 161

examined at one time sharp enough lines will be obtained upon a photographic plate mounted at OD'. For extreme spectral ranges a film in a hemi-cylindrical holder BΘ' is substituted. If an X-ray film rather than a plate is used, it may be backed with an intensifying screen to cut down the required time of exposure; but estimations of relative intensities upon the resulting photograph do not necessarily correspond to those made upon an unaided photographic emulsion.

During the course of an exposure the crystal should be moved back and forth over its prescribed path with a constant angular velocity. This is done with sufficient accuracy by a simple cam arrangement shown in Fig. 20[1]. A form of the cam itself is shown under the base of the instrument of Fig. 14.

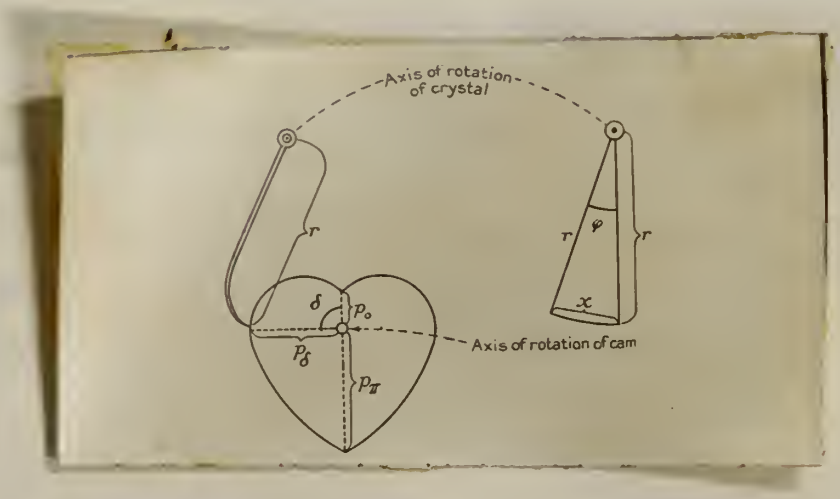

Figure 20 (Essential parts of a cam)

[1] R.W.G. Wyckoff - The Structure of Crystals, P. 162

The dimensions for any desired angle of rotation ϕ can be found. The angles expressed in radians are

$$\chi = \phi r \sim = (\rho_\pi - \rho_o)$$

where r = effective length of the rotation arm

and p_o = the smallest radius of the cam of any convenient lengths.

A constant angular velocity of rotation of the crystal will result from a constant rotation of the cam if the latter is so constructed that

$$\rho_\delta = (\rho_\pi - \rho_o)\,\delta/\pi + \rho_o$$

where δ is chosen positively and negatively from o to π. It is convenient to have at least two cams for different angular rotations. One, which should give a rotation of 20° or 30°, is useful for a general mapping of the reflections for a crystal setting. With this wide angular motion the crystal is in a position to produce any one reflection during only a small portion of its motion and consequently an exposure of several hours may be needed to record a satisfactory spectrum. It often happens that a more intimate study of a small region of the spectrum is needed; a cam giving a rotation of 5°, or less, will then be required.

A more accurate form of X-ray spectrograph for use in crystal analysis is shown in Fig. 21.[1]

[1] Wyckoff - The Structure of Crystals, P. 163

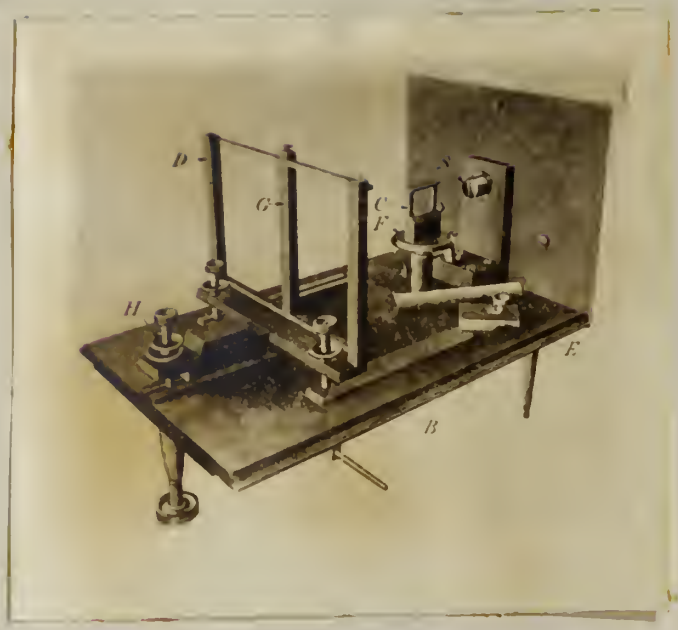

Figure 21 - (A More Accurate Form
of X-ray Spectrograph)

In this apparatus all parts are supported upon the cast metal base B. The slits are no longer adjustable but are built as a series into a removable brass tube, S. The spectrograph can be equipped with several of these tubes of various slit widths. The crystal holder is shown at c; its templet for adjusting the crystal is E. With the aid of the attached graduated circle F, and various sizes of rotation cams, it is possible to make settings for reflections from any desired spectral region. The plate holder D can be made perpendicular to the incident X-rays with the tilting screw H and a brass T (not shown), one end of which is inserted for this purpose in place of the slit tube. The removable metal block G cuts out the directly transmitted beam of X-rays. Since all accurate measurements with this instrument are comparison observations against calcite or some

other standard crystal, there is no need of measuring with precision the distance from the crystal to the photographic plate. This distance can be approximately determined with an auxiliary scale fastened upon the instrument. Its most convenient value is either five or ten centimeters, the latter being employed for accurate spacing measurements. Laue photographs also can be prepared with this same instrument by replacing the set of linear slits by a series of pin-holes and putting the section of crystal either directly over the last of these or in a suitable goniometric holder replacing C of Fig. 21.

Additional spectrographic methods have been devised as "slit-less" and "wedge" methods and seem to be better for some purposes than the ordinary spectrometric and spectrographic procedures.

Powder Spectrometry and Spectroscopy

When a thin film of crystalline powder is substituted for the single crystal of an X-ray spectrograph a diffraction pattern is obtained. If the individual crystals of this powder have no particular arrangement so that they make all possible angles with the incoming X-ray beam, all orders of reflection from all possible atomic planes have a chance to register themselves at one time. Fig. 22[1] shows the spectrum lines which result from reflections of monochomatic X-rays. This constitutes a powder photograph. During exposure the film was bent around the arc A B D of Fig. 23. The position B, of zero deflection is at the center of the photograph.

Fig. 22 (A Powder Photograph of calcite - $CaCO_3$)

If the powder is finely ground to less than about 250 mesh and its crystals have a completely unordered arrangement than a series of sharp diffraction images is obtained without rotation of the specimen. By

[1] R.W.G. Wyckoff - Structure of Crystals, P. 178

filtering the X-rays to make them essentially monochromatic such a powder pattern can be greatly simplified. Any one line is composed of reflections from only a few particles of the powder; consequently, more energy is required to produce one of these photographs than to record other X-ray diffraction phenomena. The outstanding advantage of powder diffraction methods lies in their ability to treat the many crystalline materials which do not grow large single crystals.

A number of types of spectrographs have been devised for making powder photographs. The essential parts are shown in Fig. 23[1]

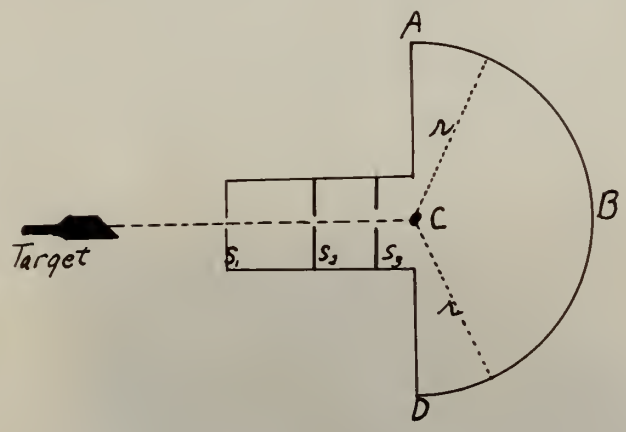

Figure 23 (Essential Parts of a Powder Spectrograph)

The X-rays from the target pass through the slits S_1 - S_3 and, striking the crystalline powder placed at C, are diffracted and recorded upon a photographic film mounted along A B D. The powder may be mounted either as a rod or a thin film, at C, on the axis of the cylindrical surface A B D. The slit system consists of a series of either pin-hole or line slits.

[1] R G W Wyckoff - Structure of Crystals, P. 179

With pin-holes the diffraction pattern is a series of curved bands. The straight and parallel lines when linear slits are used, Fig. 22, give the more accurate measurements. The width of the slits depends upon the degree of definition that is desired in the photographs. The third slit S_3 cuts off the rays diffracted by the second slit; otherwise, a diffraction pattern of the metal of this slit will be superimposed upon the lines of the crystalline powder.

A picture of a powder spectrograph of this type if shown in Fig. 24[1]. The slit system is contained within the tube S, the sample being placed directly over the inmost slit. The two outer slits are six centimeters apart, of variable width and are made from millimeter sheet gold.

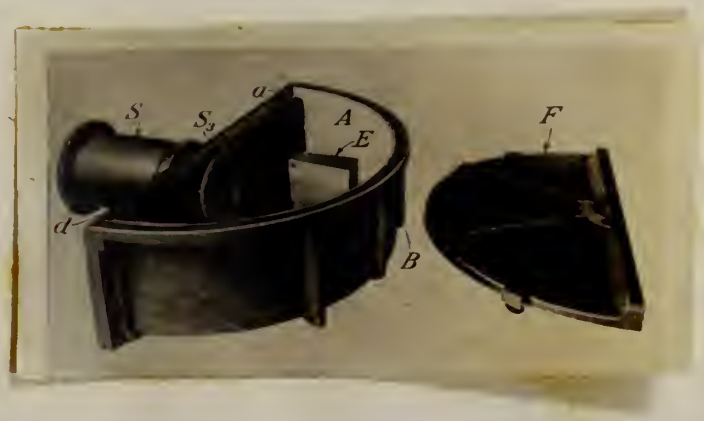

Figure 24 (Powder Spectrograph)

[1]R.W.G. Wyckoff - The Structure of Crystals, P. 180

The third slit, S_3, set three centimeters behind the second gold slit, is made of one-eighth inch brass heavily plated with gold and tapered on the inside to the edges of the slit opening which for ordinary measurements may have a width of two and a half millimeters. The body of the spectrograph and the cover (F) are copper castings, the front is a brass plate faced on the outside with sheet lead. The back, milled to form a hemicylindrical surface with its axis passing through the crystal position, may have an intensifying screen fastened to it. This screen shortens somewhat the necessary time of exposure but its effectiveness at low intensities is not great and through too great an intensification of the strong lines the pattern will not correctly be recorded. When the sensitive duplitized film is used it is put into direct contact with the screen and covered on the inside with a sheet of black paper to exclude small light leaks. Two clips a and d hold the film in place. The inverted sliding ▽, shown by E, open at the two ends and faced on the sides with thin lead, serves the double purpose of helping to hold the film in place and of protecting the film from the X-rays scattered when the directly transmitted beam strikes the film. The filtering screen may be placed either in front of the slit system S, or directly in front of the photographic plate or partly in one place and partly in the other. If only a small piece of screen is available it must be placed over the first slit. The best photographs are obtained however, by using it just before the film, for in this position it not only absorbs practically all the reflected radiation except the K-alpha lines but also most of the secondary radiations emitted by the crystalline powder. This secondary radiation is very pronounced for crystals containing elements a little lighter than the target element. The instrument can be directed towards the target by using the small

opening B; it is best placed so that the beam of X-rays used makes asmall angle with the face of the target. The radius of this sort of spectrograph is usually 10 or about 20 centimeters. Good photographs of crystals of high symmetry can be produced with the powder either contained in a fine thin-walled glass tube or spread out into a film upon paper or with collodion as a binder. When using strongly absorbing materials flour is sometimes mixed with the unknown powder.

If the number of exposures to be made simultaneously and with the same tube does not exceed two or three, spectrographs of this type are convenient and accurate but when many powder photographs are wanted as in routine checking and analytical uses when as many as 15 photographs are desired a piece of apparatus shown in Fig. 25[1] isused.

Figure 25 (A Multiple Spectrographic Outfit - after Davey)

[1]R.W.G. Wyckoff - Structure of Crystals, P. 182

The essential parts of the spectrographs are arranged as in the preceding instrument. The X-ray tube stands vertical within the metal cylinder A into which the 15 slit systems are permanently built. The first two slits, one of glass and the other of brass, serve to limit the X-ray beam; the second brass slit is a wide one designed to cut off rays scattered by the second defining slit. The holder for specimen and film is of the quadrant, as opposed to the hemi-cylindrical, type. It opens in the back for the insertion of the film which is behind the filter and is followed by a strip of intensifying screen and a brass strip to hold them in place. The undeviated beam passed through varying thicknesses of copper so that some portion of the zero line will always have an intensity comparable with that of the diffraction lines of the resulting photograph. Thefilm holders are also divided so that comparison photographs can be obtained by filling half the length of a specimen tube with one substance and the rest with another.

Powder photographs could also be made using the instrument of Fig. 19 and 21, the ionization chamber and the different "slit-less" methods of X-ray spectrography.

GENERAL RESUME OF METHOD OF DETERMINING STRUCTURES OF CRYSTALS

By using the theory of space groups all the ways of arranging the atoms of a crystal can be written down. Methods for producing and recording the diffraction effects which result when X-rays strike upon crystals have been described and equations that express, as well as may be, the influence which the arrangement of the atoms within a crystal has upon the positions and intensities of these diffraction effects have been set up. With these data at hand possible atomic groupings in crystals can be decided upon.

The essential steps of this method of crystal analysis are the following:

1. The determination of the amount of mass associated with a crystallographically possible unit cell;
2. The determination of the correct unit cell for the atomic arrangement;
3. A statement of all of the possible atomic groupings which are compatible with this unit cell and with the symmetric requirements of the crystal;
4. A selection between these possible structures through the use of the attainable diffraction data.

Whenever all of these steps are carried through, either the correct atomic arrangement in a crystal is found or, if the experimental data are insufficient to attain this end, all structures which remain possibilities are known with certainty. If one or more of these steps are omitted or

incompletely treated, as is often the case, then the resulting structure may agree with the limited experimental data that were used, but there is no assurance that it is more than one of a number of otherwise unknown possibilities.

The foregoing principles for determing crystal structure are demonstrated in the following account of the determination of the crystal structure of Magnesium Oxide, MgO.

CRYSTAL STRUCTURE OF MAGNESIUM OXIDE - MgO

Reflections from individual crystal faces, Laue photographs and powder photographs have all been obtained from magnesium oxide. Its optical behavior leaves no doubt of its cubic symmetry. A reflection spectrum photograph taken with (100) as the principal reflecting face shows that $m/n^3 = 4$. No data have been found either from interpretation of the Laue photographs or on powder photographs which require that m should be greater than 4. The crystallographic measurements available show there is no evidence that the symmetry of MgO is less than holohedial. If all cubic space groups are considered the following atomic arrangements are found to be possible.[1] In deducing these no limiting assumptions are necessary concerning the equivalence of chemically like atoms.

[1] Wyckoff, R.W.G. - The Crystal Structure of Magnesium Oxide, American Journal Science, 1, 138.

[4g, 4h] Mg atoms: 0 0 0; $\frac{1}{2}\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\frac{1}{2}\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\frac{1}{2}$,

O atoms: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $0\,\frac{3}{4}\frac{1}{4}$; $\frac{1}{4}\,0\,\frac{3}{4}$; $\frac{3}{4}\frac{1}{4}\,0$.

[4j, 4i] Mg atoms: 0 0 0; $\frac{3}{4}\frac{1}{4}\frac{1}{2}$; $\frac{1}{4}\frac{1}{2}\frac{3}{4}$; $\frac{1}{2}\frac{3}{4}\frac{1}{4}$;

O atoms: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $0\,\frac{1}{4}\frac{3}{4}$; $\frac{3}{4}\,0\,\frac{1}{4}$; $\frac{1}{4}\frac{3}{4}\,0$.

[4b, 4c] Mg atoms: 0 0 0; $\frac{1}{2}\frac{1}{2}\,0$; $\frac{1}{2}\,0\,\frac{1}{2}$; $0\,\frac{1}{2}\frac{1}{2}$,

O atoms: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $0\,0\,\frac{1}{2}$; $0\,\frac{1}{2}\,0$; $\frac{1}{2}\,0\,0$.

[4b, 4d] Mg atoms: 0 0 0; $\frac{1}{2}\frac{1}{2}\,0$; $\frac{1}{2}\,0\,\frac{1}{2}$; $0\,\frac{1}{2}\frac{1}{2}$,

O atoms: $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{4}\frac{3}{4}\frac{1}{4}$; $\frac{3}{4}\frac{1}{4}\frac{3}{4}$; $\frac{1}{4}\frac{3}{4}\frac{3}{4}$.

[4a] Mg atoms: $u\,u\,u$; $u\,\bar{u}\,\bar{u}$; $\bar{u}\,u\,u$; $\bar{u}\,\bar{u}\,u$,

O atoms: a similar term in u'.

[4 f] Mg atoms: $u\,u\,u$; $u+\frac{1}{2}, \frac{1}{2}-u, u$; $\bar{u}, u+\frac{1}{2}, \frac{1}{2}-u$; $\frac{1}{2}-u, \bar{u}, u+\frac{1}{2}$;

O atoms: a similar term in u'.

[1a, 3b Mg atoms: 0 0 0 and $0\,0\,\frac{1}{2}$; $0\,\frac{1}{2}\,0$; $\frac{1}{2}\,0\,0$

1b, 3a] O atoms: $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}\,0$; $\frac{1}{2}\,0\,\frac{1}{2}$; $0\,\frac{1}{2}\frac{1}{2}$

A study of the Laue photographic and powder photographic data shows that only planes with all odd indices give first order reflections. Calculation of the A and B terms of the intensity equation (8) indicates that arrangements [4g, 4h] and [4j, 4i] should give odd order effects from planes with two odd and one even indices; since these are not found [4g, 4h] and [4j, 4i] are impossible as structures for MgO. In arrangement [1a, 3b; 1b, 3a] reflections with two even and one odd indices, as well as those with all odd indices, should appear in the first order region; it is therefore to be eliminated from further consideration. It can also be shown that [4a] and [4 f] do not satisfy the experimental requirement of only all odd reflections in the first order unless they approach

infinitely close to either [4b, 4c] or [4b, 4d] . The choice of the correct arrangement thus lies between [4b, 4c] and [4b, 4d] .

The A and B terms of equation (8) have for [4b, 4c] the following values:

When n is odd:

If the indices are all odd, $A = 4\ \overline{Mg} - 4\ \overline{O}$, $B = 0$;

If the indices are two even and one odd or two odd and one even, $A = B = 0$;

When n is even:

$A = 4\ \overline{Mg} + 4\overline{O}'$, $B = 0$, always

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The values of A and B for [4b, 4d] are as follows:

If the indices are all odd, $A = 4\ \overline{Mg}$, $B = 4\ \overline{O}$;

If the indices are two odd and one even or two even and one odd, $A = B = 0$;

When n is 2, 6, etc.;

If the indices are all odd or two even and one odd,

$A = 4\ \overline{Mg} - 4\ \overline{O}$, $B = 0$

If the indices are two odd and one even,

$A = 4\ \overline{Mg} + 4\ \overline{O}$, $B = 0$;

When n is 4, 8, etc.:

$A = 4\ \overline{Mg} + 4\ \overline{O}$, $B = 0$, always.

10

The characteristic differences between the diffraction effects from these two structures thus lie in the relatively greater intensity of odd order reflections from 4b, 4d and in the comparative weakness of its two even and one odd and all odd reflections when n = 2, 6, etc. It is always possible to distinguish between 4b, 4c and 4b, 4d as long as the scattering power of one kind of atom in the crystal is not insignificant compared with that of the other. For this choice, powder photographic comparisons of first and second order reflections are most valuable.

In Table I the observed intensities of powder reflections from MgO are compared with those calculated by the application of (9) and (10) in the expression

$$(11)\quad I_{(hkl)} \propto j \times I_{(hkl)} = j \cdot (A^2 + B^2) \cdot \left(\frac{d_{hkl}}{n}\right)^{2.35}$$

(where j equals either the number of planes in a form or twice that number).

Table I[1] - Intensities of the Principal Powder Reflections of MgO ($\overline{Mg}$ = 12; $\overline{O}$ = 8)

Indices	Observed	Intensities Calc. for 4b, 4c	Calc. for 4b, 4d
111 (1)	2	1.75	10
100 (2)	10	10	0.4
110 (2)	9	8.8	9.1
113 (1)	2	0.5	6.5
111 (2)	5	3.6	0.1
100 (4)	3	1.9	2.0
133 (1)	0.5	0.25	3.3
120 (2)	6	6.0	0.2
112 (2)	5	4.9	5.0

[1] R.W.G. Wyckoff - The Structure of Crystals, P. 272

Magnesium and oxygen have atomic numbers so close together that the relative intensities of calculated reflections will be largely influenced by the particular values chosen for the scattering powers of these atoms. From a number of sources it seems probable that the atoms of MgO are doubly charged ions. If such is the case the electron number of each atom in this crystal is ten; if then an exact proportionality existed between the numbers of electrons in an atom and its scattering power, no first order reflections would be found from any planes. There is nevertheless good agreement between calculations for arrangement 4b, 4c , the sodium chloride arrangement (Fig. 26)[1], and observed intensities of reflection.

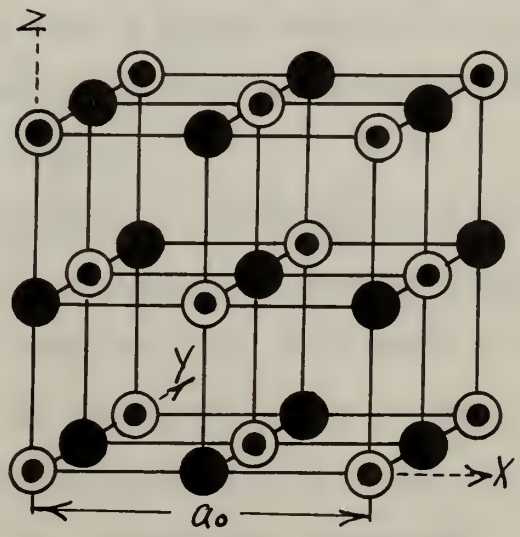
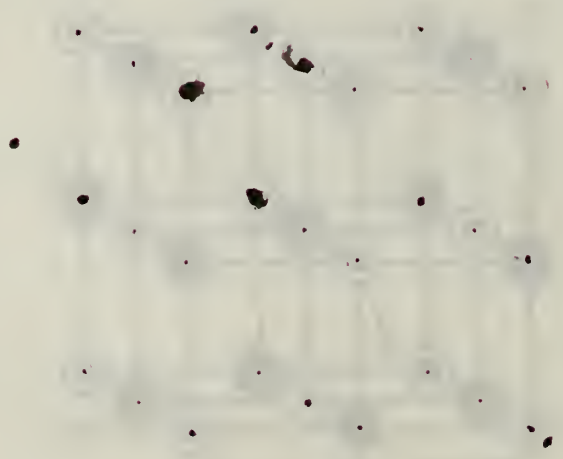


Figure 26 (The unit cube of the "sodium chloride arrangement" [4b, 4c] Either the sodium or the chlorine atoms can be represented by the ringed circles.)

It is thus clear that either this structure or an indistinguishably close approach to it must be the correct one for magnesium oxide.

Estimates of the length of the edge of the unit cube for magnesium oxide have varied from 4.22 ± o.02A° to 4.18A°; the most probable value seems to lie around 4.20A°.

[1] R.W.G. Wyckoff - The Structure of Crystals, P. 272



DIGEST

The technical difficulties confronting the use of ordinary optical diffraction gratings in the field of X-rays or Röntgen rays are due in the main to the shortness of their wave lengths. In 1912 Laue suggested that a natural crystal might serve as a three-dimensional grating for X-radiation. His idea was put to test by Friedrich and Knipping, with an apparatus as Figure 9. The experiment produced on the plate a complicated pattern of diffraction spots called a Laue diagram as in Figures 10, 11, 12, indicating clearly that Laue's suggestion was correct. The direct interpretation of these patterns as given by Laue is highly technical and complex, though the mechanism involved can be more clearly understood by the explanation offered by W. L. Bragg in 1913.

Two equations were given; the first, Eq. 5, permits the calculation of the positions of all possible diffraction effects from a crystal in terms of its symmetry characteristics, the spacing of like planes normal to some crystal face and the wave length of the X-rays; the second, Eq. 8, allows us to find the relative intensities of reflection from any plane of any distribution of atoms in a crystalline arrangement. By combining the three chief postulates with our equations and with the actual results of space group theory, as shown by the various methods for achieving patterns, it is possible to develop a systematic and more or less applicable method of crystal structure analysis.

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